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14. ABSTRACT This report results from a contract tasking Inst. of Optical Monitoring of Siberia as follows: Nonlinear optical materials are needed for use in atmospheric monitoring and remote sensing applications. ZnGeP2 is one of the most highly efficient nonlinear optical media for the middle infrared. The present proposal describes a research program to grow ZnGeP2 crystals and to investigate the relationship of "composition - crystal structure - optical properties". The latter (transparency and damage threshold) determines the use of the material in nonlinear optics. It is known that for ZnGeP2 the structural perfection is mainly determined by defects formed due to deviations from stoichiometry during synthesis and growth. Postgrowth treatment improves the physical properties of the crystals. For the Project the ZnGeP2 crystals were produced with use of two different synthesis techniques (one- and two-temperature synthesis and seeded melt and vapour growth). A vapour growth technology by the chlorine method was created and applied to grow monocrystalline layers of ZnGeP2. Postgrowth treatments were carried out for these crystals. The grown and treated crystals were characterized by optical microscopy, scanning microscopy, transmission electron microscopy, microprobe analysis, and X-ray analysis. The Russian team has significant expertise in growth of ZnGeP2 and was able to prepare the high quality ZnGeP2 crystals and carried out their assessment. They obtained new data on optical properties of ZnGeP2 and to cleared up the influence of the crystal perfection on this property. The results will have a great impact on development of modern optical devices and systems having very wide circle of applications in control and management of industrial processes as well as in ecology. Vapor growth experiments will allow data to be obtained on mechanisms of vapor growth for the ZnGeP2, and defect formation and their nature in film and volume ZnGeP2 crystals. This information will have significance for materials science, in particular, for ternary compounds, and the technology of their production.					
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**Final
Project Technical Report
of ISTC 2051-2001**

**Preparation of ZnGeP₂ for nonlinear optical applications:
melt and homoepitaxial vapor growth, properties of the grown
crystals**

(From 1 June 2001 to 29 February 2004 for 33 months)

**Alexander Ivanovich Gribenyukov
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The objective of this project in general is a solution of problem of controllable properties management by complex multi-component material, in particular by optical properties of the ZnGeP₂ single crystals which are non-linear optical material having very high potential for numerous applied spectroscopy application. The concrete problem considered in the Project is investigation of possibility to use epitaxial growth techniques for optical damage threshold decrease.

To solve the problem it was used two fundamental approaches:

- Experimental investigations of relations “production conditions” – “material composition” – “crystal structure” – “optical properties”, including epitaxial layer growth technology.
- Theoretical consideration of complex chemical vapour transport systems by methods of thermodynamic analysis.

Investigations performed in the frames of the Project have shown that at optimal temperature – concentration conditions in closed vapor transport systems with ZnCl₂ as transporting agent one can obtain epitaxial ZnGeP₂ films with smooth mirror surface. The films grown and delivered to Partner allow estimate their optical damage threshold to compare with known data obtained for volume samples.

The results of studies of physical properties of the ZnGeP₂ films grown from the vapor phase (X-Ray analysis, precise lattice parameters measurements, PL, electrical measurements) allow reveal that crystal structure of the films is more perfect than that of bulk ZnGeP₂ grown from melt. The ZnGeP₂ crystals grown from vapor have noticeable reduced total vacancy concentration. The last allows hope that the ZnGeP₂ films have increased optical damage threshold as compared with the crystals grown from melts.

KEY WORDS: Nonlinear optical crystals, II-IV-VI₂ compounds, ZnGeP₂, Melt growth, Post-growth treatments, Optical absorption, Thermodynamical analysis of gas transport epitaxial system, Vapor growth by chemical reactions, Physical properties of ZnGeP₂ films.

**The work has been performed by
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1.2 Subcontracted institutes:

Participation of subcontracted institutes was not assumed

2. Foreign Collaborators

Participation of foreign collaborators was not assumed

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Introduction

This Project relates to basic investigations in material science. It has also a great applied significance in nonlinear optics and development of different laser optical systems among which the most important are systems designated for use as remote sensors and for use in atmospheric monitoring [1].

The ZnGeP_2 single crystals are ones of the most efficient nonlinear optical media for the middle infrared. It has a wide potential optical transmission range of 0.7 to 12.5 μ , a high value of nonlinear susceptibility, and nonlinear figure of merit, what makes this material extremely attractive for incorporation in optical devices and systems

It is known that possibilities of material use in non-linear optics are mainly determined by optical transparency of the material. However, in the ZnGeP_2 there is optical absorption band related to own defects of material in the spectral range from 0.7 μ up to 2.5 μ . The absorption leads to degradation of laser frequency performance when the material is used in tuneable optical parametric oscillators (OPO) pumped by the near infrared (between 1 and 2 μ) sources. This absorption is related to deviation of composition from stoichiometry during synthesis and growth [2]. That is why the crystal properties are functioned from both synthesis technique as one of the main factors determining the beginning material composition and crystals growth conditions determining processes of defects formation and interconnection [3].

By choice of optimal crystal growth conditions and post growth treatments one can be able to improve in known limits the optical properties of the ZnGeP_2 single crystals up to level required by applications in non-linear optics.

To present development of technology for volume ZnGeP_2 single crystals production can be deemed as solved task. On base of this technology the high optical quality ZnGeP_2 single crystals were obtained. These ZnGeP_2 crystals provide fulfillment of requirements of high efficient frequency conversion of laser radiation.

Further widening of work spectral range of the converters and possibility of their miniaturization depend on success of development of vapor growth technology.

Besides, there is yet another problem related to an optical damage threshold which limited possibility to use the ZnGeP_2 crystals in high power laser systems, and consequently it reduces allowable distances for atmosphere pollutant probing. The damage threshold is related both to the surface quality (including coating) and the crystal perfection also (uniformity and thermal conductivity). In ZnGeP_2 crystals the optical break is varied in very wide range of power densities of pump radiation but the main reasons which causes it is unclear now [4].

In semiconductor physics, electronics, and microelectronics particularly, it is known that epitaxial layers compare favourably with substrates in the structure perfection and possibility to control the crystal composition. This allows suggest that application of the high optical quality ZnGeP_2 layers can solve the problems noted above. The vapour growth of ZnGeP_2 is carried out at temperatures sufficiently lower than its melting point and the suggested point of solid-solid phase transition. In this case a significant decrease in optical losses can be expected for ZnGeP_2 films as compared to the bulk crystals. Xing G.C., et al. [5] obtained an encouraging result that ZnGeP_2 grown from the vapour have practically no near infra-red absorption.

In papers concerning to studies of the OMCVD growth of ZnGeP_2 on GaP substrates [6] it was determined that ZnGeP_2 layers have high quality. Applications of such methods as chemical transport reactions [7] also give transparent, perfect crystals.

In spite of promising properties of the ZnGeP_2 epitaxial layers, till now in scientific literature there is no enough data on the ZnGeP_2 epitaxial growth to make reliable and correct conclusions about possibility of solution of the problems of volume ZnGeP_2 crystals due to growth of ZnGeP_2 films with high perfection.

OBJECTIVE OF WORK

The main goal of the Project is a solution, at least partly, of problem of controllable properties management by complex multi-component material, in particular by optical properties of the ZnGeP_2 single crystals which are non-linear optical material having very high potential for numerous applied spectroscopy application.

Work on the Project has deal with studies of possibility to grow homoepitaxial layers of the ZnGeP_2 compound by Chemical Vapour Deposition Technique (CVD).

The concrete problem of the Project was focused on investigation of possibility to use epitaxial growth techniques for controllable modification of the ZnGeP_2 single crystals optical properties. Particularly, it was assumed to investigate a possibility to increase the optical damage threshold of the ZnGeP_2 surfaces

APPROACHES

It was assumed that solution of the above noted problem will be fulfilled on base of two fundamental approaches:

- Experimental investigations of relations “production conditions” – “material composition” – “crystal structure” – “optical properties”, including epitaxial layer growth technology.
- By using the theoretical methods for thermodynamic analysis of complex chemical vapour transport systems.

MAIN TASKS OF THE PROJECT

To reach the goal of the Project it should to solve the following main task:

- Basing on known [8-10] generalized thermodynamic approach to develop computer program packet for calculations of complex chemical vapour transport systems.
- Using the computer program packet developed to estimate areas of perspective temperature-concentration parameters to grow epitaxial ZnGeP_2 layers.
- To carry out the ZnGeP_2 synthesis with use of two different synthesis techniques (one- and two-temperature synthesis).
- To grow the ZnGeP_2 single crystals for use as source and substrates in experiments on epitaxial growth of ZnGeP_2 layers.
- To carry out post-growth treatments for grown crystals.
- To perform a characterization of the grown and treated crystals and films by accessible well-known and generally recognised methods.

THERMODYNAMIC ANALYSIS OF COMPLEX CHEMICAL VAPOUR TRANSPORT SYSTEMS

Preview

Approach to the growth ZnGeP_2 layers from the vapour phase is based on the method of the chemical transport reactions. In this method a crystallised material (in our case ZnGeP_2) interacting in the source zone with other compound (transport agent) is transformed in gas compounds, which

are transported to the substrate zone with other temperature. In the substrate zone these gas compounds are decomposed according to the reverse reaction and evolve the starting material.

For reverse transport reactions it is necessary 'a priori' to know a temperature range where the initial compound will transform in a gas form as well temperatures at which compound will deposit.

Such knowledge sufficiently reduces a number of experiments to choose the optimal growth parameters. To determine the parameters "a priori" the partial pressures of all possible compounds were calculated for various temperatures. By way of selection the temperatures of zone both source and deposition and the optimal concentration of the transporting agent (chlorine in our case) are determined as well. To calculate these partial pressures a set of equations consisting of mass action laws, Dalton law, and so-called material balance equations were solved. This formalised thermodynamic model was successfully applied for various types of epitaxial systems earlier.

General scheme of solution of task of the ZnGeP₂ transportation.

One of consistent of the ZnGeP₂ is Ge, having very low volatility even at high temperatures. Therefore the main task of the ZnGeP₂ transportation is both correct choice transporting agent transforming all components of compound into vapor phase and determination of temperature ranges, which allows provide reverse chemical interaction between transporting agent and crystal to be transported.

Halogens (I, Cl, Br) are most widely used and well studied as transporting agents in epitaxial layer growth. But technological works with pure halogens present determined difficulties because halogens are toxic and very chemically active. In connection with above, in laboratory practice the compounds of halogens with own constituents of transported material are used. In case of the ZnGeP₂ transportation it should be considered as perspective transporting agents all halogenides of Zn, Ge, and P.

If the circle of transporting agents will be limited by pure halogens and their compounds with ZnGeP₂ constituents that task of thermodynamic analysis (determination of equilibrium state of thermodynamic system of four independent components) can be led to solution of the set of equations, including three material balance equations and equations binding the partial pressures of gaseous components of considered thermodynamic system.

The number of equations binding partial pressures of gaseous components is determined by the number of chemical reactions, in which gaseous components take part, reduced on the number of independent components in the thermodynamic system. These equations present the simple expressions for affinity constants for according chemical reactions. Let the chemical reaction can be written as follows:

$$\sum \nu_i A_i = 0 \quad (1)$$

where A_i are chemical symbols of compounds i , taking part in the reaction, and ν_i are stoichiometric coefficients (it is assumed that $\nu_i > 0$ for products of reaction and $\nu_i < 0$ for initial materials). Then the mass action law must have following view:

$$\prod P_i^{\nu_i} = K(T) \quad (2)$$

where $K(T)$ is affinity constant, P_i are partial pressures of compounds A_i . Activities of condensed participants of the chemical reaction are assumed equal to 1.

Numerical values of the affinity constants are determined via changes of thermodynamic Gibbs potential ΔG_i in course of the reaction

$$RT \ln K_i(T) = -\Delta G_i \quad (3)$$

$$\Delta G_i = \Delta H_i - T \Delta S_i \quad (4)$$

where ΔH_i and ΔS_i are changes of enthalpy and an entropy, respectively, R is a gas constant, T is a temperature.

All thermodynamic values are calculated due to known data about thermodynamic properties of elements and their compounds [11-13].

As the material balance equations needed for complete description of thermodynamic system state either Dalton Law (if it is known the total pressure in the system) or its pared-down form related to transporting agent only as well as ratios between components resulted from stoichiometry of compound to be transported.

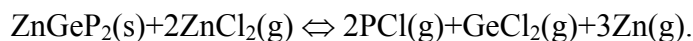
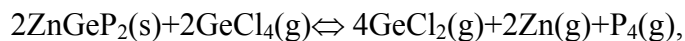
Brief review of the results of thermodynamic analysis for closed gas transport systems Zn-Ge-P-Cl (ZnGeP₂-ZnCl₂) and Zn-Ge-P-I (ZnGeP₂-I₂).

Taking in account view of equations (2), it is clear that the complete set of equations is nonlinear. The analytical form of solution is impossible for such sets of equations. Therefore the set of equations makes to use numerical methods of solutions. For calculation of thermodynamic equilibrium one can apply known Newton-Rafson iteration procedure [14].

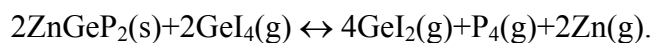
The only condensed phase, namely stoichiometric ZnGeP₂, was taken in account at calculations thermodynamic equilibrium of the systems Zn-Ge-P-Cl (ZnGeP₂-ZnCl₂) and Zn-Ge-P-I (ZnGeP₂-I₂). It was assumed that vapor phase can be formed by 13 constituents: Zn, ZnCl, ZnCl₂, GeCl, GeCl₂, GeCl₄, P₂, P₄, PCl, PCl₃, PCl₅, Cl, Cl₂ in case of usage Cl (or ZnCl₂) as a transporting agent. The analogical constituents of vapor phase were taken in account for calculations of system with iodine.

Basing on calculations of the temperature dependences of Gibbs potential changes ΔG in course of reaction for all reactions, which can realize between the condensed phase and vapor phase components, we have concluded that the ZnGeP₂ transport is possible in both systems as in system with chlorine (or ZnCl₂) as well as in system with iodine.

Analysis performed shows that in the system with chlorine the ZnGeP₂ transport is provided due to two reversible reactions:



In the system with iodine the transportation can be described by one of basic reactions:



By using numerical methods of calculations the partial pressures of all gaseous components were calculated as functions of the temperature. It was found that in the system

Zn-Ge-P-Cl the total pressure is determined by the four components of vapor phase: ZnCl₂, GeCl₂, GeCl₄, and PCl.

Analysis fulfilled allowed choose temperature ranges for both nutrient zone and substrates zone and estimate the range of the transporting agent concentration perspective for ZnGeP₂ layer growth..

In the system Zn-Ge-P-I the total pressure is formed by the five components of the vapor phase: P₂I₄, ZnI₂, GeI₂, GeI₄, PI₃. It was concluded that the ZnGeP₂ transport by using iodine shall to have more complex character as compared with the chlorine system.

EXPERIMENTAL DETAILS

Preview

At the Project performance it was suggested the application of the technical approaches which are widely used in semiconductor material science for production of bulk crystals and films.

Particularly it was assumed:

1. To synthesis the ZnGeP_2 compound from the elements by using two techniques of synthesis, such as two-temperature method developed by the project participants as well as one-temperature method known from scientific publications;
2. To grow the ZnGeP_2 single crystals by using of the seeded vertical Bridgman (VB) method;
3. To fulfill the after-growth thermal treatments of the grown ingots;
4. To perform additional treatment of the wafers by fast e-beam.

Detailed description of synthesis, growth, and post-growth treatments of bulk ZnGeP_2 crystals is in our earlier Report [15].

ZnGeP_2 synthesis

Polycrystalline ZnGeP_2 was synthesised from the elements using the two-temperature furnace titled 10 degrees to horizon. The furnace is described in [16].

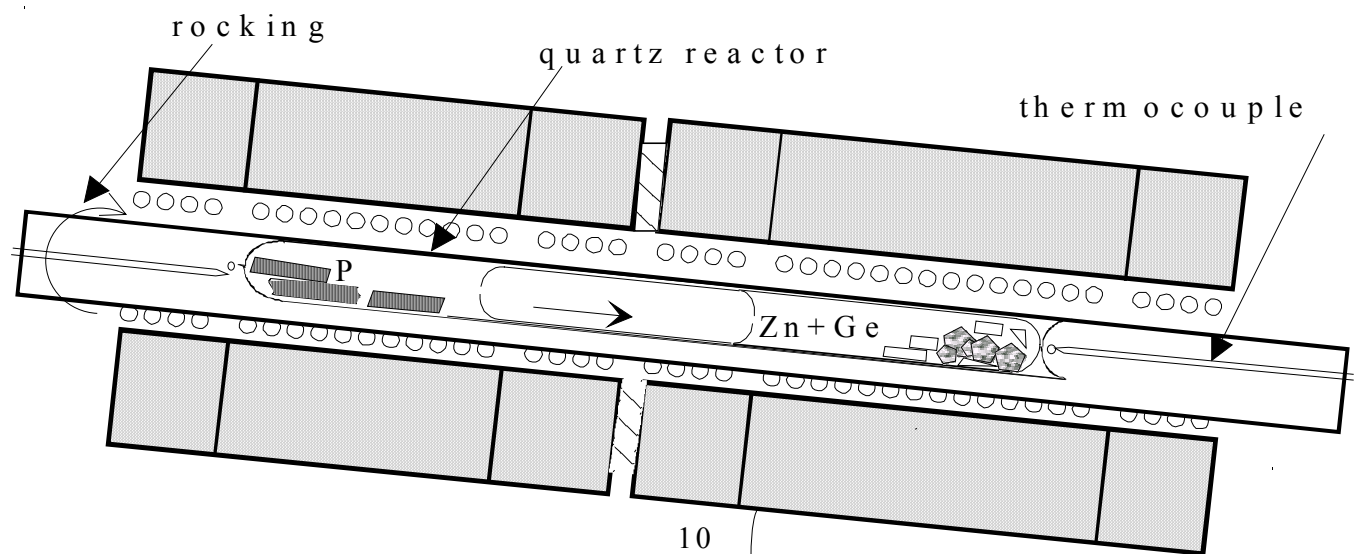


Fig. 1. Schematic of a furnace and synthesis reactor

In two-temperature process, phosphorus from the cold zone of the two-zone furnace is transported to a mixture of zinc and germanium in the hot zone. Initially, the Zn/Ge alloy's temperature is raised to 1010 °C (~17 °C below the melting point of ZnGeP_2), whilst the cold-zone temperature is raised to 520 °C to provide the dynamic flow of phosphorus and to raise the phosphorus pressure to 10.5 atmospheres to suppress the out-diffusion of zinc from the Zn/Ge alloy and the formation of zinc phosphides in the cold zone. Once the P transport to the Zn/Ge alloy is completed (~10 hours) the ZnGeP_2 is heated to 1050 °C and the now-empty P- zone is heated to 1060 °C to transport any volatile components to the melt zone. Real time-temperature regime for ZnGeP_2 synthesis is presented in Fig.2 and also in [17].

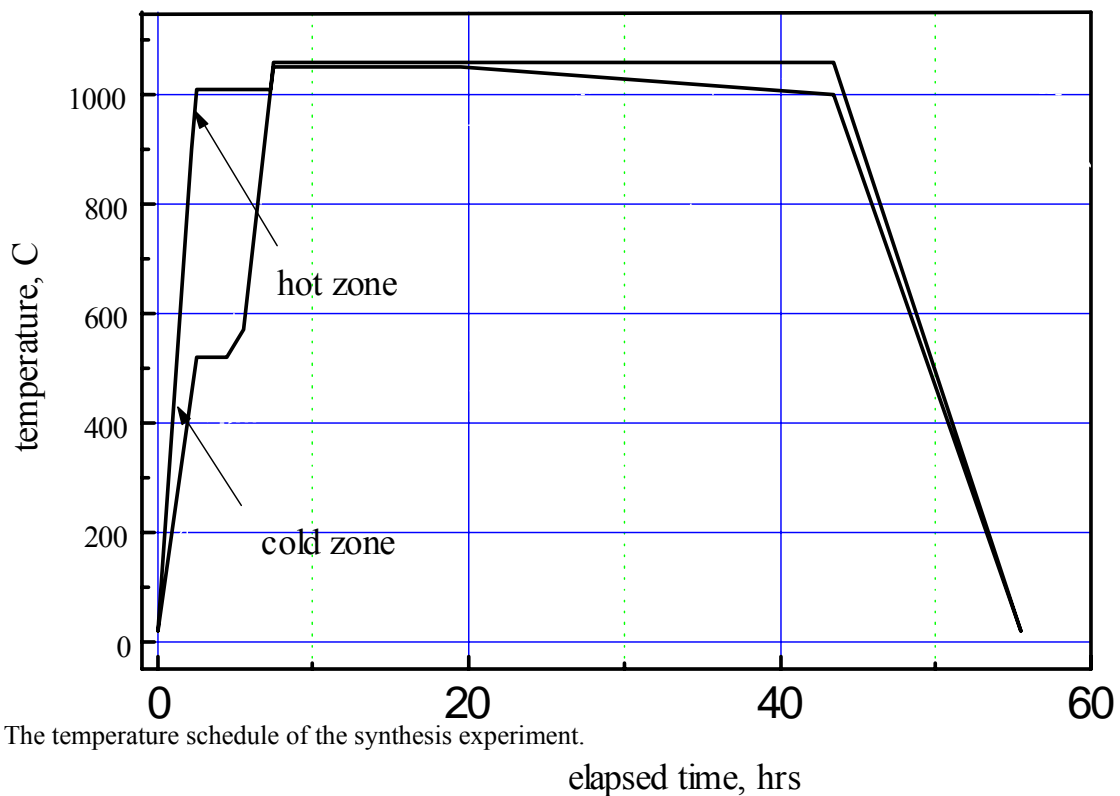


Fig. 2. The temperature schedule of the synthesis experiment.

As to one-temperature synthesis that all three initial elements are placed in one zone which are originally heated to 550-600 °C only to bind the pure P with Zn and exclude its high vapour pressure at heating to higher temperatures when the ZnP_2 compound will react with Ge to form ZnGeP_2 . The reaction rate between the P and Zn is much lower at these temperatures, so the method does not allow provide a big amount of the material. In our experiments we use charges weighting not more 100 gm.

Crystal growth

A vertical Bridgman technique was used for ZnGeP_2 single crystal growth. Schematic of the growth container and temperature profile is shown in Fig. 3.

The temperatures of the upper and lower zones are 1060°C and 1000°C , respectively. The temperature gradient is $2\text{--}3^\circ\text{C}/\text{cm}$ near the melting point (1027°C). The ampoule translation rate could be varied from 0.5 mm/hour up to 4 mm/hour .

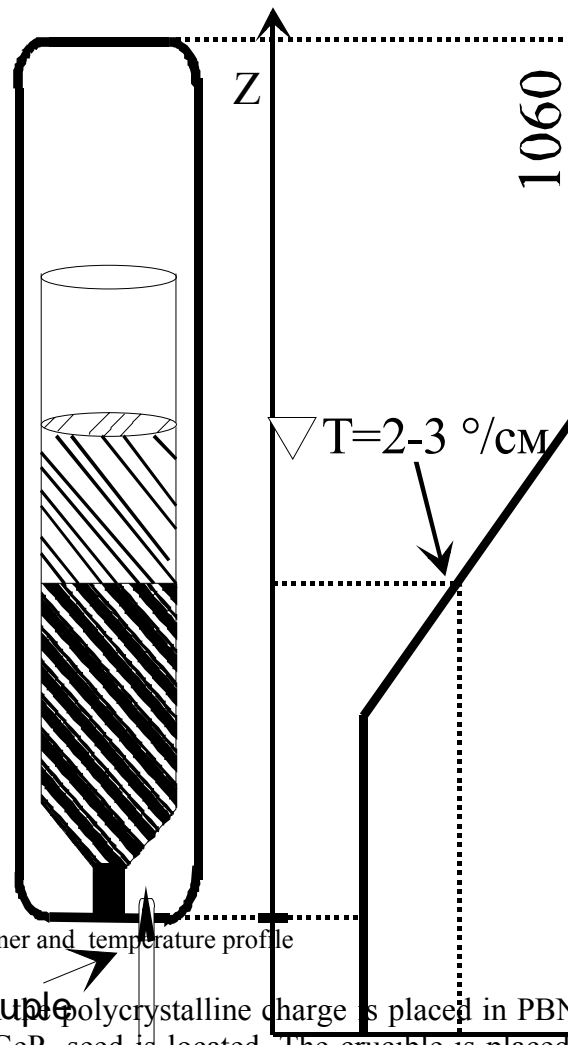


Fig.3 Schematic of the growth container and temperature profile

After the chemical polycrystalline charge is placed in PBN growth crucible, in the bottom of the crucible the ZnGeP_2 seed is located. The crucible is placed in the quartz container, which then evacuated and sealed. The container is placed in the upper hot-zone to provide the charge fusion and partial fusion of the seed. After soaking the container is slowly pulled down through the temperature gradient.

Thermal annealing

Post-growth thermal annealing is ordinary used to improve the optical properties of ZnGeP_2 crystals.

Thermal treatment allows reduce the optical absorption at $2\text{ }\mu\text{m}$ down to values of $0.1\text{--}0.2\text{ cm}^{-1}$, permitting the fabrication of OPO's pumped by laser radiation in this spectral range.

To remove stresses formed at crystal growth (the stresses can lead to cracking of a crystal during cutting) all crystals were annealed in uncut state.

Typical regime used for annealing was following: temperature - 600 °C, duration - 400 hrs, atmosphere – vacuum nominally.

Before annealing the crystals were preliminary etched in a warm (~70 °C) mixture of acids HNO₃: HCl = 1:1 for 5-7 min. After etching, the crystals were carefully washed and dried, placed in quartz ampoules, which were evacuated down to pressures of 10⁻⁶ atm and then sealed. To prevent possible thermal shocks a heating and cooling of the ampoules was carried out together with furnaces.

E- beam irradiation.

In general experiments on e-beam irradiation were described in our Report [15] and published papers [18, 19]. The energy of electrons was ~3.9 MeV. The samples were irradiated for approximately 40 hours to obtain the integral e-beam flux of about $1.5 \cdot 10^{17} \text{ cm}^{-2}$. At such electron energy the penetration depth of electrons was about 3 mm, so the irradiation from one side was enough to create uniform distribution of radiation introduced defects in the samples with thickness less than 3 mm.

Optical measurements and optical data treatment.

A two beam spectrophotometer SPECORD M80 (Produced by “Karl Zeiss”, Iena, Germany) was used to record optical transmission in the spectral range 2.5 - 12 μ. For measurements at shorter wavelengths (0.7-2.6 μ) a spectrophotometer for luminescence analysis, “SDL 3”, produced by St.-Petersburg optical mechanical association (former “LOMO”) was used. The latter is a single-beam instrument.

It should be noted that the SPECORD M80 is not optimized for work with samples such as ZnGeP₂ having high optical density (refractive index more than 1.5). In addition, the inaccuracy increases with reduction of a sample thickness, and with increasing error in the parallelism and flatness of the optical surfaces of the sample. Typically, random error in measurements is less than 2 % but systematic errors from the causes noted above can be much higher, necessitating calibration against an external source. Calibration was therefore performed using the single-beam configuration and a He-Ne laser (at 3.39 μm).

In absence of equipment for spot measurements of absorption at fixed laser frequencies and with known polarization, we have applied a method of determination of the ordinary and extraordinary optical absorption coefficients based on optical transmission measurements using typical spectrophotometers with unpolarized radiation [20]. The basic principles, algorithms, and calculation sequence were presented in [15].

Vapour growth of ZnGeP₂ films.

According to the calculations we carried out earlier [21] the ZnGeP₂ transport with use of chlorine as transporting agent seems to be more simple and efficient as compared with iodine transport. These circumstances have affected on choosing of chlorine (or ZnCl₂) as transporting agent.

ZnCl₂ was produced by reaction between the elemental Zn and HCl; both components were of high purity. After dissolution of Zn in HCl the residual part of HCl and H₂O were evaporated and a dry ZnCl₂ was formed. The dry ZnCl₂ was then placed in the ampoules, which then were sealed because of the high hygroscopicity of this chloride.

Before the experiments the growth ampoules were treated in Aqua Regia during 48 hours, then carefully washed in deionised water and dried.

As a nutrient a single crystalline pieces of ZnGeP_2 were taken. Single crystalline polished plates of ZnGeP_2 with thickness of ~ 1 mm and orientations of (508) or (100) were taken as substrates. Before charging in the growth ampoule the nutrient and the substrate were etched in $\text{HCl}:\text{HNO}_3=1:1$ then washed and dried. Also for substrates another etchant ($\text{HNO}_3:\text{HF}:\text{CH}_3\text{COOH}:\text{I}_2=2\text{ml}:2\text{ml}:1\text{ml}:2\text{mg}$) was sometimes applied to study an effect of etching agent on the substrate surface. Pure elemental phosphorus was also charged into the growth ampoules to create equilibrium pressure above the substrate during growth.

The nutrient and the substrate were weighed before and after growth experiment to determine losses or increase in weight. After evacuating down to 10^{-6} atm and sealing the ampoule was placed in preliminary heated furnace.

Typical temperature profiles created in the furnace are shown in Fig.4.

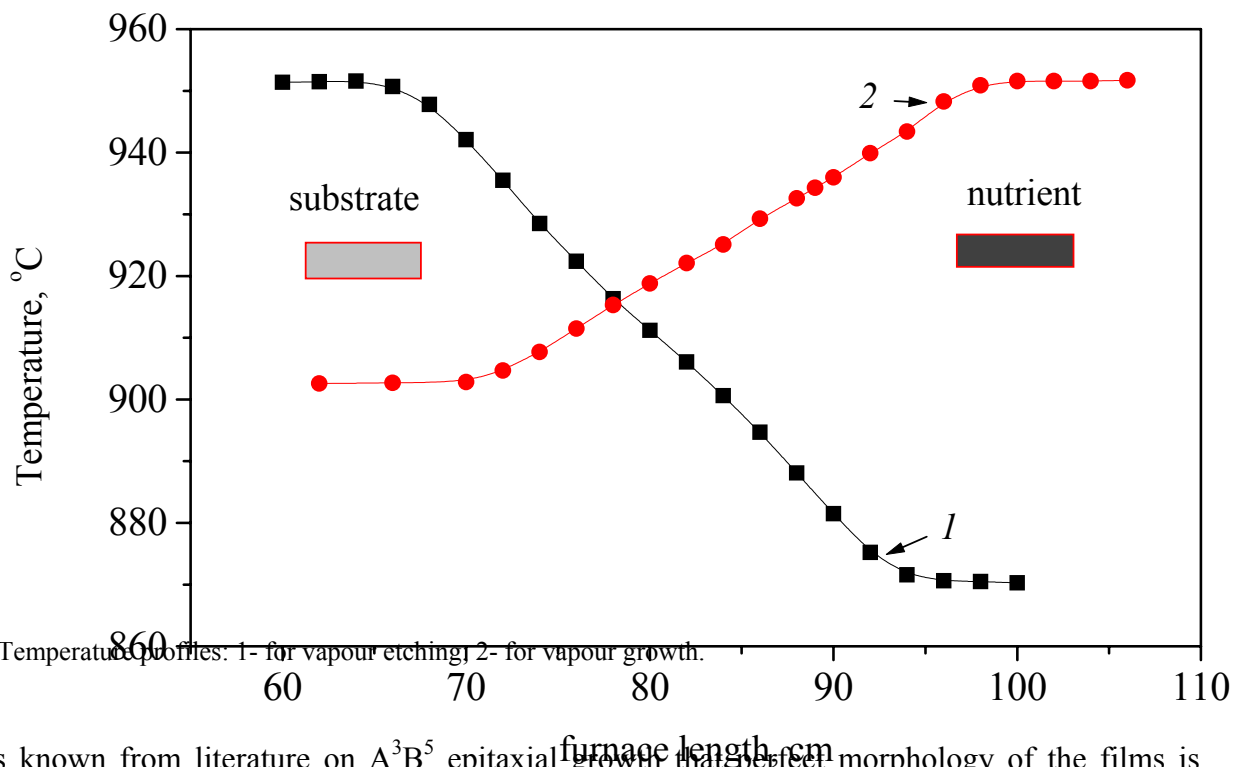


Fig.4. Temperature profiles: 1- for vapour etching; 2- for vapour growth.

It is known from literature on A^3B^5 epitaxial growth that perfect morphology of the films is provided by two-dimensional growth, which is realized through movement of steps or their trains. A limited rate of the material transport toward the growth zone results, as a rule, in formation of three-dimensional nuclei. The nuclei growth can lead to formation of growth islands, and consequently, to imperfection of the growing layer. To provide the two-dimensional growth it was

necessary to create such growth conditions when a quantity of the transporting material is enough for formation of two-dimensional nuclei (steps). In doing so, however, the transport rate should not exceed a value, which can lead to achievement of so-called growth in saturation regime since in this case a perfection of the growing layer is degraded.

In order to determine optimum conditions (from the point of view of surface perfection) for ZnGeP_2 layers growth the temperatures and chlorine concentration were varied during growth experiments.

Zinc chloride charges added in the ampoules were varied to create in volume the initial concentration of $0.1\text{--}2\text{ mg/cm}^3$.

The temperatures of the nutrient and growth (substrate) zones were varied from 970°C to 900°C and from 910°C to 850°C correspondingly.

Optical properties of the volume ZnGeP₂

Typical optical absorption spectrum of as-grown ZnGeP₂ sample is presented in Fig. 5.

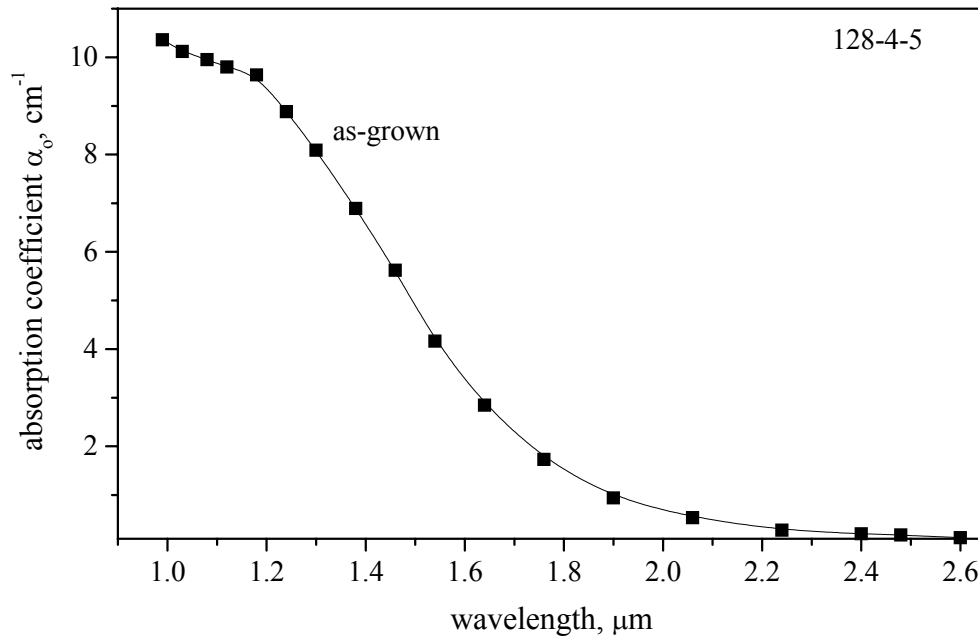


Fig. 5. Absorption coefficient spectrum of as-grown ZnGeP₂ single crystalline sample #128-4-5 for optical ray with ordinary polarization.

Optical absorption coefficient in area of maximal transparency (3-8 μm) of ZnGeP₂ single crystals can be less than 0.05 cm⁻¹ in absence of inclusions which are caused by divergences of the crystal composition from stoichiometry. The inclusions give non-selective reduction of transparency of crystals and lead to degradation of optical absorption coefficient. In the range near 2 μm presenting interest for pump of OPO based on ZnGeP₂ crystals one can indicate that optical absorption coefficient values are in the interval from 0.4 cm⁻¹ to 1.2 cm⁻¹. Even more are data scattering for the optical absorption coefficient nearly 1 μm: from 6 cm⁻¹ up to 12 cm⁻¹.

Fast e-beam irradiation of as-grown ZnGeP₂ crystals allows reduce the ordinary ray optical absorption coefficient down to values of about 0.2 cm⁻¹, what is not enough to create the high-efficient OPO pumped by radiation with wavelength near 2 μm.

Thermal annealing of as-grown ZnGeP₂ crystals allows us to reduce the optical absorption more sufficiently as compared with the fast e-beam irradiation. Annealing allows to obtain samples with optical losses at 2 μm as low as 0.08 - 0.3 cm⁻¹, but yield of samples with absorption level of 0.08 - 0.1 cm⁻¹ is rather low and it is not superior 25-30 %.

Only joint effect of both thermal anneals and fast e-beam irradiations gives stable result with high yield. Due to e-beam irradiation of preliminary annealed ZnGeP₂ samples one can reduce the optical losses down to level of 0.03-0.01 cm⁻¹ at 2 μm.

The typical behaviour of optical absorption spectrum at the ZnGeP₂ anneals and following fast e-beam irradiation is shown in Fig. 6.

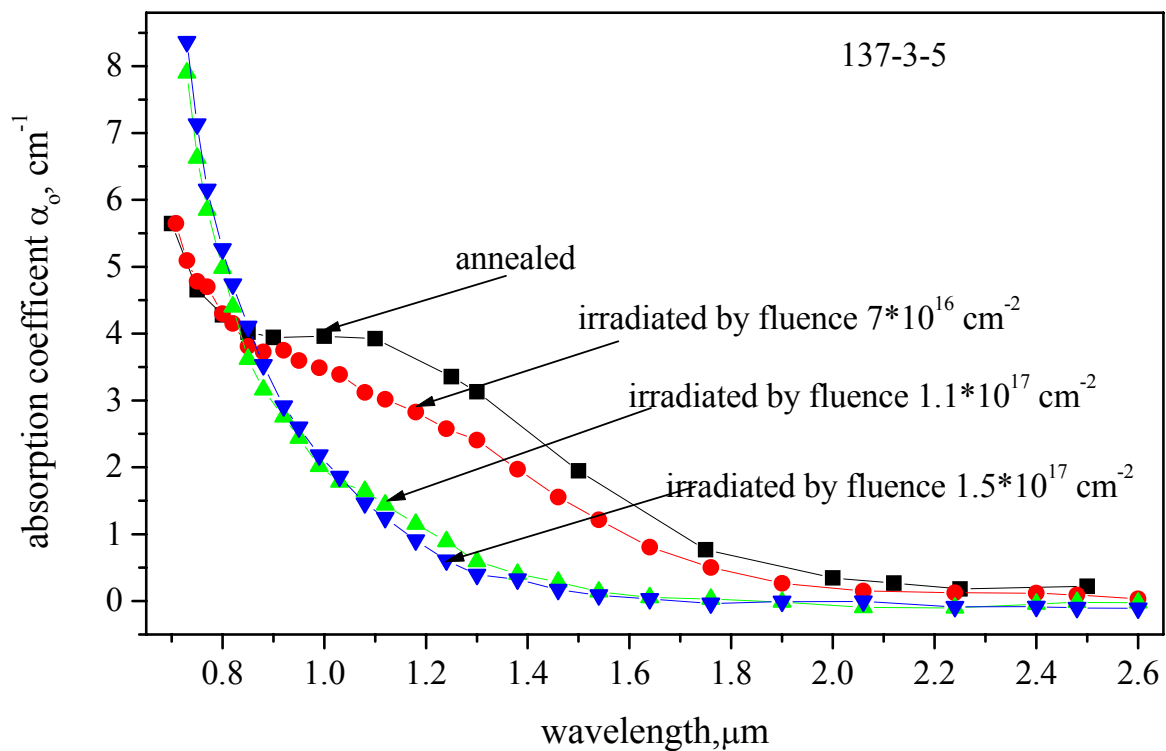


Fig.6. Ordinary ray absorption coefficient spectrum for the ZnGeP_2 sample #137-3-5 in annealed state and after e-beam irradiation by several fluencies.

Vapour growth of the ZnGeP_2 , properties of the films

First epitaxial growth experiments showed that ZnGeP_2 layers had a semi-mirror surface. It was proposed that type of the surface could be determined not only by complex structure of the substrate crystallographic plane (508) but also by three-dimensional nucleation. Therefore, it was necessary to increase the transport rate of ZnGeP_2 material to transfer to two-dimensional growth. To this aim it was planned to increase the chlorine concentration, nutrient temperature, and temperature gradient between the nutrient and growth zones as well.

However, under the experimental conditions providing increased transportation rate it was indicated that transported material deposits on substrates only partly. In Fig.7 is presented the real temperature profiles used in experiments on the ZnGeP_2 layers deposition in closed chlorine CVD system.

With use of the profile #1 (minimal temperature gradient and respectively assumed minimal transportation rate) only 1/3 part of transported material of nutrient deposits on ZnGeP_2 substrate, its 2/3 parts deposits on ampoule walls. With increase of temperature gradient (profiles #2 and #3) a greater part of the transported material deposits on the ampoule walls but not on the substrate.

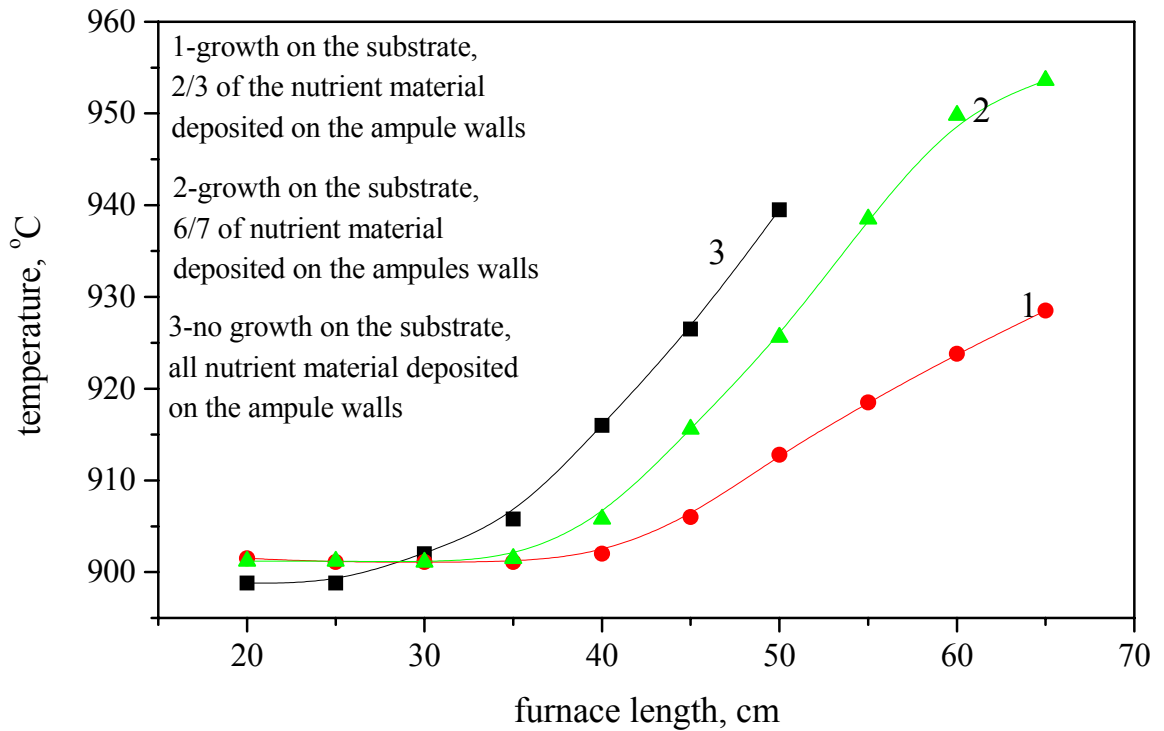


Fig. 7. Real temperature profiles for vapour growth

With temperature profile #2, only 1/7 parts of the nutrient material deposits on the substrate another part deposits on the ampoule walls. Profile # 3 does not provide growth on the substrate; there is a slight etching of the substrate, and all nutrient material deposits on the ampoule walls.

Experimentally it was determined that region of the material deposition depends on a curvature of a used temperature profile; this is on sign and value of a second derivative of temperature with respect to coordinate. Schematically this is shown in Fig. 8.

Nevertheless, some epitaxial films, 3-70 μm in thickness, were grown by chemical transport reactions with use of ZnCl_2 as transporting agent in a closed gas transport system. The estimated growth rate of the ZnGeP_2 layers was about 1.2 $\mu\text{m}/\text{hour}$.

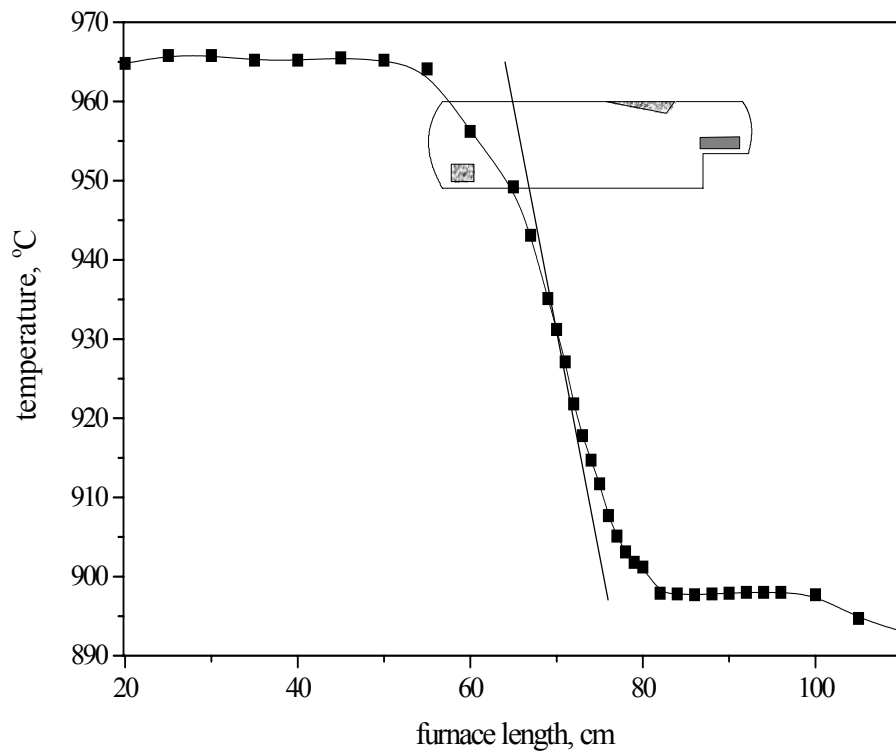


Fig.8. Temperature profile for vapour growth and schematic of the growth ampoule.

Properties of the grown ZnGeP_2 films.

Properties of the grown films were studied by X-Ray analysis, microscopy, PL, and electrical parameters were also measured. Comparison with properties of the bulk crystals has been carried out.

X-Ray analysis.

X-Ray analysis of vapour grown material was carried out for material deposited on the ampule walls and for layer grown on the substrate. In both cases it was revealed that material corresponded only to one phase, namely, ZnGeP_2 . The deposited ZnGeP_2 has the following crystallographic lattice parameters: $a = b = 0.54656 \pm 0.00002$ nm and $c = 1.07114 \pm 0.00005$ nm. These data showed some increased values as compared with ordinary ZnGeP_2 crystals grown from melt: $a = b = 0.54650 \pm 0.00002$ nm and $c = 1.07088 \pm 0.00005$ nm. Thus X-ray measurements have shown that the unit cell volume of vapor grown ZnGeP_2 is bigger than that of melt grown. The relative change of measured unit cell volume dV/V is 0.00047 ± 0.00025 .

A character of the Laue pattern of the grown films shows that the film is single crystalline and there are no other phases.

Next Fig.9 presents angular half-widths of diffraction peaks depending on interplanar spacing d for ZnGeP_2 crystals grown from the melt and from the vapor. It is seen that the half-widths for the vapor grown material are narrower than those for the bulk crystals that shows a lower level of point defects. The narrower half-widths for vapor grown material can be related to a decrease in total vacancy concentration as compared with bulk material

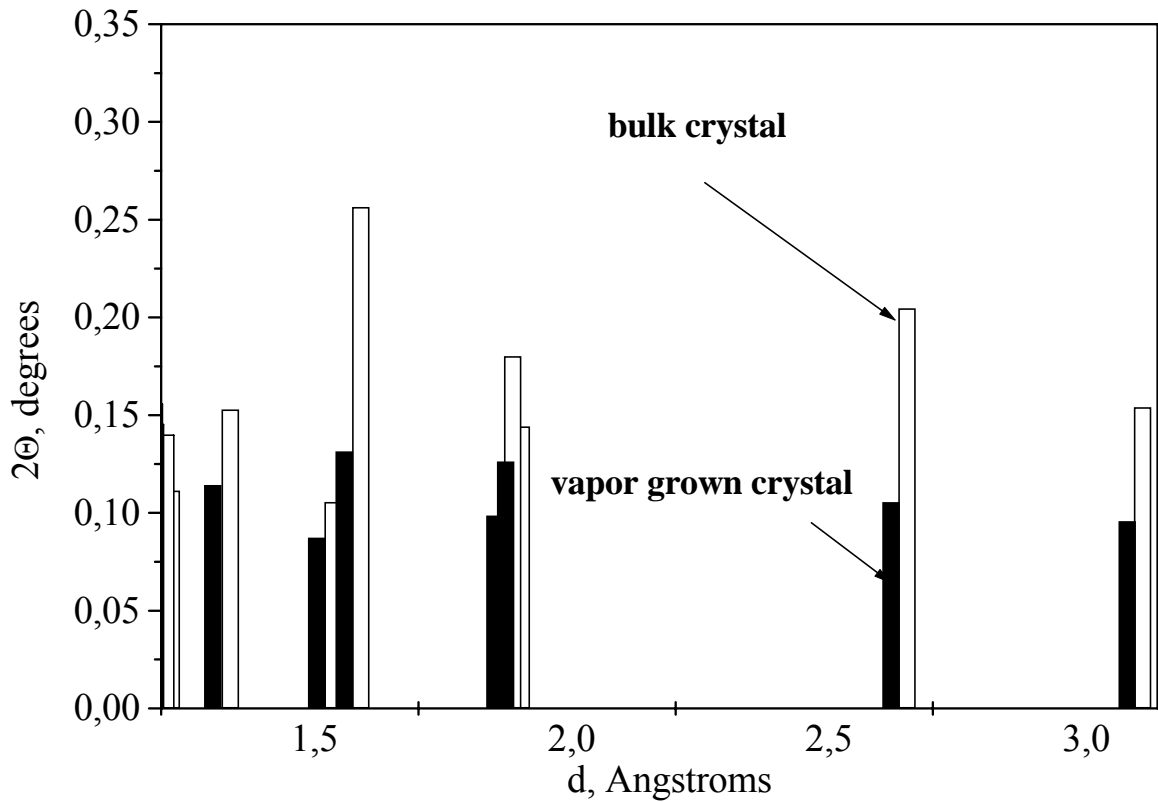


Fig.9. Angular half-widths $\Delta\Theta$ depending on interplanar spacing d for ZnGeP_2 , grown by different methods.

It is known that formation of vacancies leads to local increase of interatomic distances around empty vacancy center (so-called distortion effect) and to reduction of average interplanar distances in macroscopic scale.

Estimation of near-vacancy distortion was made in paper of L. Halliburton et.al. [22]. In accordance with the data from this paper the linear near-vacancy distortion along principal c -axis is 20 %. Assuming that changes of macroscopic parameters are isotropic (including the changes related both to formation and to disappearance of vacancies) a non-compensated volume of vacancy as a fraction of volume occupied by atom can be estimated as $V_{\text{vacancy}}/V_{\text{unit}} = 0.8 \times 0.8 \times 0.9 = 0.576$. Thus, substitution of vacancies by atoms must result in increase of measured values of unit cell volume on

$$\frac{V_{\text{atom}} - V_{\text{vacancy}}}{V_{\text{atom}}} = \frac{1 - 0.576}{1} = 0.424$$

To provide the relative change of unit cell volume dV/V on 0.00047 (see Table 1) it is necessary to allocate atoms instead vacancies with fraction Δ of $0.00047 / 0.424 = 0.0011$ of total amount (number) of ideal atomic positions in crystal.

Taking in account that the molar weight of ZnGeP_2 M_{ZnGeP_2} is 199.96 g, the density of ZnGeP_2 ρ_{ZnGeP_2} is 4.15 g/cm³, and the Avogadro number N_A is $6.02 \cdot 10^{23} \text{ mol}^{-1}$, the vacancy concentration

reduction $\Delta C_{\text{vacancy}}$ in vapor grown ZnGeP_2 as compared with melt grown material can be estimated as:

$$\Delta C_{\text{vacancy}} = \frac{\Delta \cdot N_A \cdot \rho_{\text{ZnGeP}_2}}{M_{\text{ZnGeP}_2}} = \frac{0.0011 \cdot 6.02 \cdot 10^{23} \cdot 4.15}{199.96} = 1.4 \cdot 10^{19} \text{ cm}^{-3}$$

This estimation is close to equilibrium vacancy concentration in ZnGeP_2 calculated from thermodynamics [23]. This allows believe that the change in lattice parameters is really related to change in the vacancy concentration since concentrations of point defects of disordering or substitution are much lower than those of vacancies. Besides, the distortion of the lattice near these defects is also lower as compared with that due to the vacancies, and therefore, more wide variations in change of point defect concentrations are necessary to reach the observed increase in lattice parameters.

Our conclusion about reduction in the total vacancy concentration in the vapor grown ZnGeP_2 is in a good agreement with PL data.

Photoluminescence

Fig.10 depicts photoluminescence spectra for bulk and film ZnGeP_2 material. Measured PL spectra for bulk ZnGeP_2 present a wide emission band in 0.7-1.5 eV region, consisting of two overridden elementary bands with maximums at 0.9 and 1.2 eV. According to [24] an emitting transition with energy ~ 1.2 eV is usually attributed to point defects of vacancy type, emission in 0.9-1.0 eV is related to disorder defects in cation sublattice Ge_{Zn} . It is seen from the spectra that luminescence intensities in 0.9 eV region are practically the same for bulk and vapor grown crystals. However, the emission band with maximum at 1.2 eV, dominating in the spectra of bulk material, is highly weakened in the spectra of the vapor grown material.

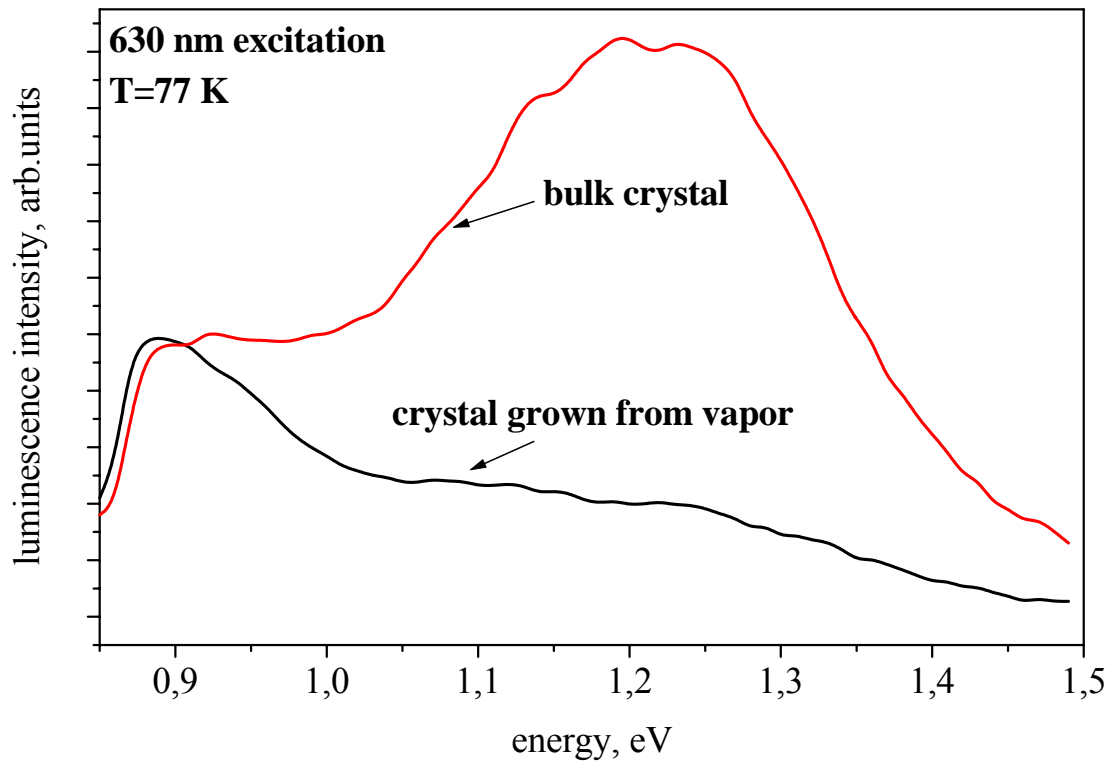


Fig.10. Photoluminescence spectra measured at 77K for ZnGeP_2 , grown from the melt and from the vapor.

Electrical properties are the main characteristics of materials, determining the use of these materials in semiconductor electronics. In case of optical materials the measurements of electrical properties can be useful for estimation of a defect concentration and their potential influence on optical absorption.

Specific electrical resistivity was measured by Van der Pauw method with use of ZnGeP_2 samples of rectangular shape with contacts obtained by melting of In on purified (by etching) surface of samples at 340 °C during 10 minutes. Simultaneously with the resistivity a Hall effect was measured using a standard 4-sonder scheme. Magnetic intensity was 4100 Oe.

The measurements were carried out for bulk material, which was used for the substrates (122/1/20) and homoepitaxial structure (K-41). For the structure (K-41) the measurements were made from two sides: from the side of the layer and from the opposite side to compare substrate and layer properties. The results of electrical measurements for bulk crystal and epitaxial structure are presented in Table 2. Comparison of properties of bulk crystal and epitaxial structure shows that during vapor growth a free holes concentration p increases, and mobility μ decreases.

Table 2. Electrical properties of ZnGeP_2 .

<i>ZnGeP₂ sample parameters</i>	Bulk crystal 122/1/20	Substrate K-41	Layer K-41	
<i>Thickness, cm</i>	0.08	0.11	0.0060	0.11
Hole concentration p, cm^{-3} ,	5.64×10^9	1.45×10^{10}	1.84×10^{11}	1.00×10^{10}
Hall mobility $\mu, \text{cm}^2 \cdot \text{V}^{-1} \cdot \text{sec}^{-1}$	71.4	45.6	52.2	52.2
Resistivity $R_o, \Omega \cdot \text{cm}$	1.55×10^7	9.44×10^6	6.50×10^5	1.19×10^7
Hall constant $R_H, \text{cm}^3/\text{C}$	1.11×10^9	4.31×10^8	3.40×10^7	6.22×10^8

Such behavior of electrical parameters is typical for bulk ZnGeP_2 , annealed in a temperature interval 850-1000 °C [24]. A usage of real thickness of the layer 60 μm gives a sufficiently higher value of the holes concentration than in the substrate, whereas the calculated value of the mobility is also higher as compared with the substrate. Untypical behavior of mobility (its increase) with increase of the holes concentration disappears if the total thickness of the structure will be used instead of the layer thickness. Thus, from electrical measurements the following conclusion can be made: true electrical parameters of the layer material are apparently shunted by the substrate, and therefore, the layer material should have equal or higher resistivity than the substrate

Morphology

Morphology studies of the ZnGeP_2 films grown during the first Phase of the Project were described in our Third Intermediate Report [15].

The studies have shown that the ZnGeP_2 films grown on substrates with orientation (508) have numerous scattering defects. These growth imperfections are clearly seen and result in semi-mirror surfaces. An estimation of average value of roughness along casual direction gave the mean value of roughness about 21 nm.

Semi-mirror character of the grown layers could be related to both non-optimal growth thermal conditions and unfavorable complex structure of surface planes of substrates oriented as (508).

To check influence of the ZnGeP_2 substrates crystallographic orientation on grown layers morphology we have performed some experiments with (100) orientation substrates.

As it turns out the films grown on (100) substrates appear more mirror-like as compared with layers grown on (508) substrates. But the tunnel microscopy studies show that the average height of roughness is higher on 30 % for films grown on substrate with (100) orientation as compared with

films grown on substrates with (508) orientation. Thus the mirror-like reflection of light from ZnGeP₂ films with (100) orientation should be related to sizes of area of roughness, which differs more than in 2 times as compared with the film of (508) orientation.

Further vapor phase growth experiments were focused on attempts to produce the ZnGeP₂ films with mirror smooth surfaces due to growth conditions.

As it was noted above, it was found, that the ZnGeP₂ transportation rate and quantity of deposited material are sufficiently depend on both temperature gradient created in the closed CVD system and values of the second derivative of temperature on coordinate, i. e. temperature distribution curvature in fixed point.

To understand and then to find the conditions of the perfect ZGP film growth from vapor it is necessary to consider moving forces acting on transport flows of the main gaseous constituents existing in Zn-Ge-P-Cl gas transport system at non-isothermic conditions.

Gases mixture flows analysis for non-isothermic conditions

Stationary transport flows

In stationary case, when detail equilibrium is in effect, all molecules flow according each to another and general transport rate is determined (limited or managed) by flow of gaseous component having the lowest transport rate.

To find the component limiting transport process in case of the ZnGeP₂-ZnCl₂ system let consider the simplified case (of one-dimensional diffusion flow) the flow density j created by diffusion of particles (gas molecules) can be written by well-known 1-st Fick's Law:

$$j = -D * (dn/dx) \quad (5)$$

where D is diffusion coefficient and dn/dx is derivative of the gas molecules density (concentration) on linear coordinate.

Taking in account that the thermodynamically balanced molecules density (concentration) is depending on temperature, the expression (5) can be converted in following one:

$$j = -D * (dn/dT) * (dT/dx) \quad (6)$$

where dn/dT is derivative of the molecules density (concentration) on temperature and dT/dx is temperature gradient in determined point of considered part of the transport system.

To compare flow densities of different kind molecules one can use ratio:

$$j_k/j_m = D_k/D_m * (dn_k/dT)/(dn_m/dT) \quad (7)$$

As it is seen from expression (7) the ratio of flows densities depends on only temperature values, but it is independent from temperature gradient in considered point.

Thus, in closed gas transport systems, where transport is determined by diffusion of molecules, the component limiting the gas transport rate cannot be changed by variation of temperature profile (distribution) in furnace

As it was shown earlier in our Second Intermediate Report [21] the main gaseous components in closed Zn-Ge-P-Cl gas transport system are ZnCl₂, GeCl₂, GeCl₄, and PCl.

An example of the calculations result is presented in Fig.11.

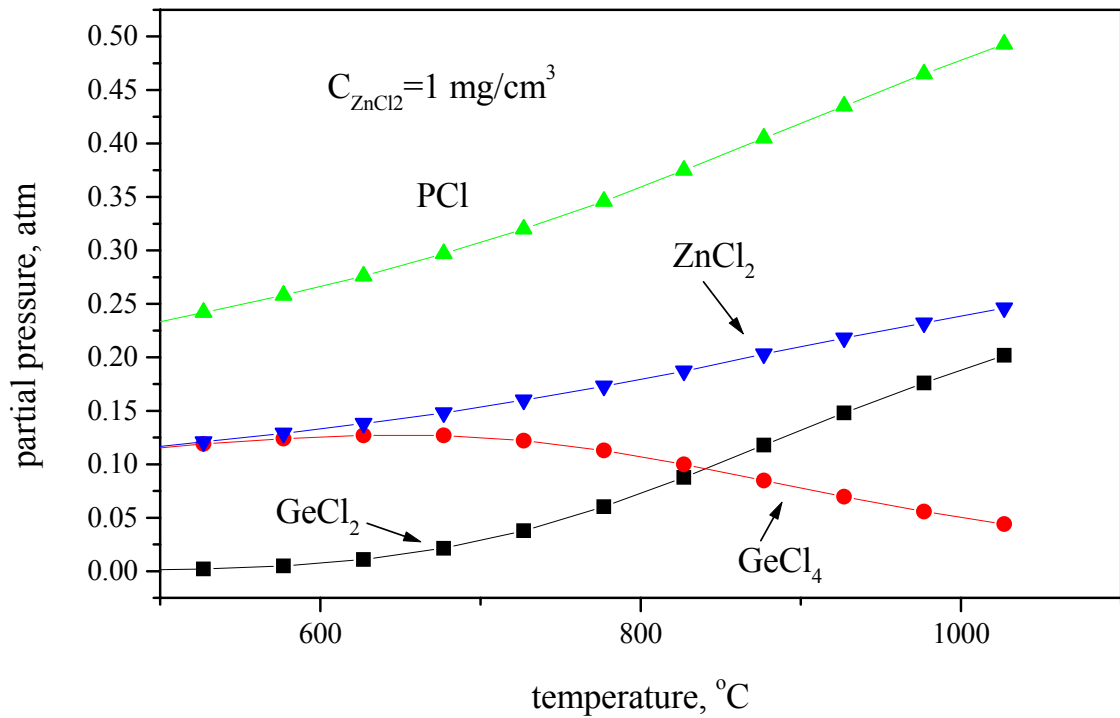


Fig. 11. Partial pressures of gas compounds over ZnGeP_2 in Zn-Ge-P-Cl system with $C_{\text{ZnCl}_2}=1\text{ mg/cm}^3$. (Taken from the 2-nd Interim Report [21])

These results show that concentrations (partial pressures) of PCl and ZnCl_2 in Zn-Ge-P-Cl system are significantly higher than GeCl_2 and GeCl_4 , therefore it is reasonable to compare the flows densities ratio for the last components.

Assuming the reciprocal diffusion coefficients dependence from weight of molecules, one can estimate the ratio of diffusion coefficients as following:

$$D_{\text{GeCl}_2} / D_{\text{GeCl}_4} = (72.5 + 4 \cdot 35.45) / (72.5 + 2 \cdot 35.45) = 1.5.$$

To create one molecule of GeCl_4 it takes to use two molecules of GeCl_2 , therefore for estimation relative efficiency of these molecules flows one should consider expression:

$$R = (0.5 \cdot j_{\text{GeCl}_2} / j_{\text{GeCl}_4}) = 0.5 \cdot 1.5 \cdot (dn_{\text{GeCl}_2} / dT) / (dn_{\text{GeCl}_4} / dT).$$

The ratios R were calculated as functions of initial concentration of the transporting agent ZnCl_2 and presented in Fig. 12.

As it is seen at all concentrations (partial pressures) of transporting agent the component GeCl_4 gives less flow density as compared with GeCl_2 . Thus GeCl_4 is the component limiting transport ZGP in gas transport system. It is seen also that the ratio is weak function of temperature at ZnCl_2 concentration within interval $1.5 - 3.0 \text{ mg/cm}^3$.

To check possibility a change of the limiting component due to the presence of additional free phosphorus charges in transport system it was made calculations with material balance equation, in which the ratio of Zn (or Ge) to P is varied. These calculations showed that the used variable do not change practically foregoing analysis results.



Fig. 12. Ratio of flow densities for GeCl_2 and GeCl_4 at different concentration of gas transport agent in the closed transport system: R03, R05, R07, R10, R15 and R30 accord to ZnCl_2 concentration (partial pressure) as 0.3, 0.5, 0.7, 1.0, 1.5, 3.0 mg/cm³, respectively.

Deposition

The gas flow with changed density (concentration) of molecules is described by the 2-nd Fick's Law:

$$\partial C / \partial t = -D * \text{div}(C) = -D * (\partial^2 C / \partial x^2) \quad (8)$$

where $\partial C / \partial t$ is partial derivative of component concentration on time (by other words: it is component deposition/generation rate), $\partial^2 C / \partial x^2$ is the second partial derivative of component on linear coordinate, accordingly.

Applying the same principles of differentiation as above (see (7)) one can obtain:

$$(\partial C / \partial t) = -D * \partial / \partial x [\partial C / \partial T * \partial T / \partial x] = -D * [\partial^2 C / \partial T^2 * (\partial T / \partial x)^2 + \partial C / \partial T * \partial^2 T / \partial x^2] \quad (9)$$

This expression shows evidently the direct dependence deposition rate from both temperature gradient and temperature profile curvature.

Strictly speaking, in non-isothermic conditions the gaseous components concentrations must differ with them calculated for the thermodynamically balanced state. Besides, the rates of both chemical etching and deposition on substrates can have limitations near surface region.

In general, influence of the temperature gradients will not proportional to influence of the temperature profile curvature. Therefore as work dependence should use corrected expression (9):

$$(\partial C / \partial t) = -A * \partial^2 C / \partial T^2 * (\partial T / \partial x)^2 - B * \partial C / \partial T * \partial^2 T / \partial x^2 \quad (10)$$

where A and B are parameters, which shell to be determined from empiric data.

It takes high reliable thermal equipment with high repeatability of temperature distributions to do correct estimations of these parameters, which are functions of nutrient temperature, substrate temperature, and possibly the transport agent concentration.

During the Project execution the thermal equipment required for epitaxial growth experiments was created. An example of temperature distributions was presented in description of the vapor growth experimental details (See Fig.4).

The last ZnGeP_2 films delivered to Partner look as mirrors, in spite of the presence some scattering centers.

CONCLUSION

Basing on the results of work performed in the frames of Partner Project ISTC № 2051p/EOARD#00-7041, one can make the following conclusion:

1. The synthesis of polycrystalline ZnGeP_2 in two variants has been carried out:
 - By using the two-temperature technique developed by the project participants it was synthesised 400 g of polycrystalline ZnGeP_2 ;
 - By the one- temperature technique known from literature data it was was synthesised 400 g of the ZnGeP_2 compound.
2. On base of technology developed in IOM SD RAS 3 (three) single crystals of the ZnGeP_2 have been grown. The seeded vertical Bridgman (VB) method was applied for growth of ZnGeP_2 single crystals with high optical quality
3. Main parts of the crystals obtained were annealed.
4. As-grown and annealed parts of ZnGeP_2 crystals were used to prepare oriented wafers for experimental studies of vapor phase transport process and CVD ZnGeP_2 layers.
5. Part of the prepared substrates was irradiated by fast (4 MeV) electrons.
6. The planned comparative investigations of optical properties (transmission and absorption) for ZnGeP_2 crystals obtained on different stages of technology: after growth, after post-growth anneals, and after fast e-beam irradiation have been performed.
It was found that both thermal annealing and irradiation by fast electrons allows sufficiently reduce initial optical absorption in defect related spectral range of as-grown ZnGeP_2 single crystals:
 - Electron irradiation decreases the absorption down to values about 0.2 cm^{-1} at $2 \mu\text{m}$;
 - Annealing allows decrease the $2 \mu\text{m}$ absorption down to $0.08\text{-}0.3 \text{ cm}^{-1}$;
 - Combined treatment gives the excellent result and allows reach the optical losses level less then 0.03 cm^{-1} at $2 \mu\text{m}$.
7. All substrates planned for experimental studies of optical damage threshold depending on the ZnGeP_2 treatment stages have been delivered to Partner in proper time.
8. It was considered the known generalized methods of thermodynamic analysis typically used for studies of quasi-equilibrium processes in multi-component systems, which could be applicable for solution of tasks related to the ZnGeP_2 transportation via vapor phase.
9. It was founded a scheme of solution of transport task and its mathematical formulation. The Newton-Rafson technique was chosen to solve the equation net consisted of the mass action laws, Dalton Law and material balance equations.

10. It was developed and described the principal block-diagram for solution of thermodynamic task for vapor phase transport of complex chemical compounds in the closed system.
11. To realize the developed block-diagram it was created the general computer program packet for calculations of different parameters of chemical vapour transport systems for complex multi-component compounds.
12. Control and test of the program packet was fulfilled by using known data for well-studied gases.
13. The program packet was applied for calculations of thermodynamic equilibrium of constituents of the vapor phase for CVD systems including the ZnGeP_2 and various transport agents.
It was considered both opened system $\text{ZnGeP}_2\text{-HCl-H}_2$ and closed systems $\text{ZnGeP}_2\text{-ZnCl}_2$, $\text{ZnGeP}_2\text{-HCl}$, $\text{ZnGeP}_2\text{-I}_2$. Performed calculations of the vapour phase composition in opened and closed systems with various transport agents and partial pressures of the gas constituents for isothermal mixtures showed that all of considered systems can be applied to the ZnGeP_2 vapour growth.
Comparison of calculation data on the efficiency of the systems
 Zn - Ge - P - Cl (ZnCl_2) and Zn - Ge - P - I allowed make conclusion about preferences of the chlorine system.
14. It has been found that in the Zn-Ge-P-Cl system a total pressure is mainly created by ZnCl_2 , GeCl_2 , GeCl_4 , and PCl . The perspective temperature regions for epitaxial ZnGeP_2 layers growth have been estimated as dependences of transport agent concentration.
15. The first experimental circle on ZnGeP_2 vapor transport was performed with use of following transporting agents: ZnCl_2 , I_2 . It was performed X-ray powder analysis and precise lattice measurements for product of CV transport of ZnGeP_2 .
The studies showed that transported material has chalcopyrite structure and corresponds to ZnGeP_2 of stoichiometric composition.
16. The second series of 28 experiments on ZnGeP_2 transport has been executed with ZnCl_2 as transporting agent.
Single crystalline ZnGeP_2 layers were grown on substrates both (100) and (508) orientations.
In first time the precise measurements of lattice parameters of the ZnGeP_2 crystals grown from vapor phase were performed.
17. Comparison of the half-widths and lattice parameters of the bulk and film ZnGeP_2 allows conclude that ZnGeP_2 grown from the vapor has lower concentration of vacancies than the bulk crystals grown from the melt. Estimation gives that the reduction of summary vacancy concentration in the vapor grown ZnGeP_2 is close to the equilibrium one calculated from thermodynamic principles.
18. It was performed the PL studies of the ZnGeP_2 films. The results of the PL studies are consistent with data of X-ray investigations. The emission transition attributed to vacancies in ZnGeP_2 is significantly less pronounced for the vapor grown material as compared with melt-grown ZnGeP_2 .
19. The electrical measurements carried out have been shown that the vapor grown ZnGeP_2 layers have equal or higher resistivity as compared with substrates.

20. The second series of experiments on the ZnGeP_2 vapor growth showed that the mass of compound deposited on substrates is strongly depends on temperature profile in transporting system. To explain the results obtained it was considered transport flows of the main gaseous constituents existing in Zn-Ge-P-Cl gas transport system at non-isothermic conditions.
21. It was carried out 42 experiments on vapor growth of ZnGeP_2 films with using of ZnCl_2 as transporting agents and under varied temperature conditions in working space source-substrate. In result of these experiments it was obtained some mirror-like ZnGeP_2 films appropriate for optical damage measurements.
22. All planned deliveries substrates and homoepitaxial structures and Reports were performed completely.
23. It was made the scientific Report on MRS Fall Meeting 2002 (Boston, MA, USA).
24. Some of Results of work on the Project were published [26,27].

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27. G.A.Verozubova, A.I.Gribenyukov, M.C. Ohmer, N.C. Fernelius, J.T. Goldstein. “Growth and characterization of epitaxial films of ZnGeP₂”, Mat.Res.Soc.Symp.Proc., (2003), vol. 744, pp. 561 – 567, Editors: Bradley D. Weaver, M.Omar Manasreh, Chennupati Jagadish, Stefan Zollner

LIST OF PUBLISHED PAPERS AND REPORTS WITH ABSTRACTS**PAPERS**

1. G.A. Verozubova, A.I. Gribenyukov, V.V. Korotkova, A.W. Vere, C.J. Flynn – ZnGeP₂ growth: melt non-stoichiometry and defect substructure – J. of Crystal Growth, 237-239, p. 2000-2004, (2002)

Abstract

A real defect structure is studied for ZnGeP₂ crystals grown by vertical Bridgman technique from the melt. Optical microscopy finds growth striation and precipitation of second phases emerging because of deviation from stoichiometry. The revealed growth striae have a complex structure caused by temperature oscillations in a growth setup. The other type of defects, precipitates, is observed as a colony of the trails oriented in longitudinal direction. The colony of trails occurs with a concave interface and as a rule, is located in the central part of the lateral section of crystal. The most probable composition of the precipitates is a mixture of ZnGeP₂, Zn₃P₂, and Ge. The colony of the precipitate trails results in significant optical losses over whole transparency range of ZnGeP₂.

2. A.I. Gribenyukov, G.A. Verozubova, A.Yu. Trofimov, N.T. Yunda – Formation of uniform point defect distribution in ZnGeP₂ single crystals at fast e-beam irradiation – Proceedings of 6-th International Conference on Modification of Materials with Particle Beams and Plasma Flow, 23-28 September 2002, Tomsk, Russia, p.311- 314.

Abstract

The results of distribution profile calculations for point defects occurring in ZnGeP₂ samples under fast e-beam irradiation are presented using two different estimates of the binding energy of atoms in the crystal lattice. The use of a binding energy of 25.15eV derived from the averaged bond energies in the compound gives good agreement between calculated and observed irradiation defect distribution profiles. In contrast, we conclude that the value of binding energy for Zn atoms in ZnGeP₂ derived from data on nearest neighbour Zn-P bond strengths leads to an underestimate. . Approximation of the calculated irradiation defect profiles by Gaussian distributions allows us to define the irradiation regimes producing ZnGeP₂ samples with electrical non-uniformity less than 10 %

3. G.A. Verozubova, A.I. Gribenyukov, M.C. Ohmer, N.C. Fernelius, J.T. Goldstein. “Growth and characterization of epitaxial films of ZnGeP₂”, Mat.Res.Soc.Symp.Proc., (2003), vol. 744, pp. 561 – 567, Editors: Bradley D. Weaver, M.Omar Manasreh, Chennupati Jagadish, Stefan Zollner

Abstract

Thermodynamic analysis of the vapor phase over ZnGeP₂ in Zn-Ge-P-Cl system has been carried out. The calculations (analysis) showed that this system can be used for the vapor growth of ZnGeP₂. Homoepitaxial layers of ZnGeP₂ were grown in a closed system using chemical vapor transport. Electrical and photoluminescence properties of the layers were studied, and crystal lattice parameters were measured. Comparison of properties for bulk and vapor grown ZnGeP₂ crystals were carried out. It was found that the vapor grown crystals has more perfect structure than the bulk ones, particularly, they have significantly lower vacancy concentration.

4. A.I. Gribenyukov, G.A. Verozubova, A. Yu. Trofimov, A.W. Vere, C.J. Flynn. “Native point defect interaction in ZGP crystals under influence of e-beam irradiation”, Mat.Res.Soc.Symp.Proc., (2003), vol. 744, pp. 315 – 320, Editors: Bradley D. Weaver, M.Omar Manasreh, Chennupati Jagadish, Stefan Zollner

Abstract

Optical absorption in defect-related region of high-efficient non-linear ZGP crystals under e-beam irradiation and post-irradiation anneals has been investigated.

It was found partly irreversible changes of the absorption in spectral range 0.9-2.5 μm (0.5-1.3 eV) at effect of the irradiation and subsequent low-temperature anneals. Data obtained are in contradiction with vacancy nature of the ZGP absorption in the 0.5-1.3 eV range.

The least square fit for parameters of theoretical dependence of optical absorption cross-section to experimentally measured ZGP optical absorption coefficient spectra results in conclusion that the defect-related absorption in 0.5-1.3 eV region is caused by deep donor levels with energy position $E = E_v + 0.9 \text{ eV}$.

Significant changes of the energy spectrum of dominant optically active centers have been indicated under influence of e-beam irradiation and post-irradiation anneals.

Founding on the optical absorption measurements data obtained for as-grown, annealed and e-irradiated ZGP crystals, model of point defects interaction taking in account both reversible interactions such as formation of donor-acceptor pairs and irreversible interactions of quasi-chemical type has been proposed.

Behavior of optically active defects energy spectrum is discussed in frames of the model of interaction between the initial point defects and radiation ones.

Analysis performed showed that the best agreement with experimental data is reached when it is assumed that optical defect-related absorption in the 0.5-1.3 eV range related mainly to the disordering defect in cation sublattice of ZGP, namely, to atoms Ge substituting Zn.

Defect concentration profiles created by e-irradiation in ZGP crystals of different thickness were calculated. It was found the conditions providing uniformity of defect distribution on dept of irradiated ZGP samples.

The optimal e-beam irradiation flux, giving maximum of ZGP enlightenment, allowed us to reduce the defect-related absorption down to value 0.01 cm^{-1} at 2 μm

REPORTS

1. The first Intermediate Report on Partner Agreement #2051/ EOARD #00-7041 (Registration No. 0497/01/01in STIII of MS&T) "Preparation of ZnGeP_2 for nonlinear optical applications: melt and homoepitaxial vapour growth": THERMODYNAMIC ANALYSIS OF GAS TRANSPORT SYSTEMS: VAPOR GROWTH OF ZnGeP_2

ABSTRACT

Present Report consists of 29 pages, including 4 Tables, 2 Figures, 13 References.

KEY WORDS: NONLINEAR OPTICAL CRYSTALS, II-IV-VI₂ COMPOUNDS, ZnGeP_2 , THERMODYNAMICAL ANALYSIS, GAS TRANSPORT EPITAXIAL SYSTEM.

The present Report consists of three sections. The first section includes description of generalized thermodynamic model of quasi-equilibrium process, typical for gas transport systems.

The second section contains a mathematical apparatus, adequate to the thermodynamic model, and allowing to obtain a full information about thermodynamical state of the system.

The third section shows examples of application of generalized thermodynamic model and mathematical apparatus for consideration of potential gas transport systems for vapor growth of ZnGeP_2 . The transport system ZnGeP_2 - HCl seems to be the most interesting for ZnGeP_2 vapor growth.

2. The Second Intermediate Report on Partner Agreement ISTC #2051/ EOARD #00-7041 (Registration No. 0497/01/01in STIII of MS&T) "Preparation of ZnGeP_2 for non-linear optical applications: melt and homoepitaxial vapour growth": GAS TRANSPORT SYSTEMS FOR ZnGeP_2 GROWTH: THERMODYNAMIC CALCULATIONS AND ANALYSIS OF VAPOR PHASE COMPOSITION.

ABSTRACT

Present Report consists of 36 pages, including 11 Tables, 18 Figures, 10 References.

PROJECT TECHNICAL REPORT

KEY WORDS: NONLINEAR OPTICAL CRYSTALS, CHALCOPYRITE COMPOUNDS, ZnGeP_2 , THERMODYNAMICAL ANALYSIS OF GAS TRANSPORT EPITAXIAL SYSTEM, VAPOR GROWTH BY CHEMICAL REACTIONS.

The present Report consists of two sections. The first section shows results on thermodynamic calculations and analysis for gas transport system Zn-Ge-P-Cl, and the second section shows the results and analysis for Zn-Ge-P-I system. Such thermodynamic analysis has been carried out for systems “ ZnGeP_2 - halogen” for the first time.

Changes of the Gibbs potential for possible chemical reactions in systems Zn-Ge-P-transporting agent have been calculated and the reactions of transport have been found for both systems.

With use of developed computer program partial pressures of gas compounds in these systems have been calculated. On base of the partial pressures a factor of efficiency of transporting agent has been built. Analysis of the efficiency factor behaviour depending on temperature and concentration of transporting agent allowed to choose technological parameters for vapour growth of ZnGeP_2 for both systems

3. The Third Intermediate Report on Partner Agreement ISTC#2051/ EOARD #00-7041 (Registration No. 0497/01/01 in STII of MS&T) "Preparation of ZnGeP_2 for nonlinear optical applications: melt and homoepitaxial vapour growth": ZnGeP_2 MELT AND VAPOR GROWTH: TECHNOLOGY AND PROPERTIES OF THE GROWN CRYSTALS

ABSTRACT

The Report consists of 40 pages, including 2 Tables, 33 Figures, 12 References, and 2 Appendices

KEY WORDS: NONLINEAR OPTICAL CRYSTALS, ZnGeP_2 , SYNTHESIS AND GROWTH OF BULK CRYSTALS FROM MELT, VAPOR GROWTH BY CHEMICAL REACTIONS.

The present Report consists of two sections. The first sections describes technology on synthesis, growth, and post-growth treatments of bulk ZnGeP_2 crystals and their optical properties. As post-growth treatments a thermal annealing and e-beam irradiation by 4 MeV electrons have been applied. Optical absorption data show that thermal annealing decreases the absorption coefficient down to values within interval of $0.08 - 0.3 \text{ cm}^{-1}$ at $2 \mu\text{m}$, whereas the electron irradiation can reduce the coefficient to values lower then 0.03 cm^{-1} .

The second section is devoted to ZnGeP_2 growth from the vapor phase and physical properties of the grown films. A technology of vapor growth by chemical transport reactions is described. X-Ray analysis, PL, electrical measurements and microscopy have been applied for study of physical properties of the ZnGeP_2 films. It has been revealed that crystal structure of the films is more perfect than that of bulk ZnGeP_2 grown from melt.

LIST OF PRESENTATIONS AT CONFERENCES AND MEETINGS WITH ABSTRACTS

1. International Quantum Electronics Conference (IQEC/LAT 2002), 22-27 June 2002, Moscow, Russia,

Report: “ ZnGeP_2 growth for nonlinear applications” by G.A.Verozubova, A.I. Gribenyukov, V.V. Korotkova

ABSTRACT

In present paper problems of fabrications of transparent ZnGeP_2 crystals are considered: synthesis, growth defects. The defects have a negative impact on optical transparency. Post-growth treatments allow to reduce the absorption down to 0.01 cm^{-1} at $2 \mu\text{m}$.

2. International Quantum Electronics Conference (IQEC/Lat 2002), 22-27 June 2002, Moscow, Russia,

Report: "Low optical losses ZnGeP₂ crystals for high efficient OPO pumped by 2 mkm lasers" by A.I. Gribenyukov, G.A. Verozubova, A.Yu. Trofimov, A.W. Vere, C. J. Flynn

ABSTRACT

Behaviour of optical absorption in ZnGeP₂ were studied under the effect of post-growth thermal anneal and e-beam irradiation. Irreversible changes of spectra were found under e-beam irradiation that are explained by interaction of primary defects with irradiation ones.

3. IX Joint International Symposium "Atmospheric and Ocean Optics, Atmospheric Physics", Tomsk, Russia, 2 – 5 July 2002

Report "ZnGeP₂ crystals for applied spectroscopy: optical quality test by IR thermovision" by A.I. Gribenyukov, G.A. Verozubova, V. V. Korotkova, A. Yu. Trofimov, V. V. Reyno, M. V. Sherstobitov

ABSTRACT

ZnGeP₂ single crystals are attractive material for radiation frequency conversion in the middle IR region. Nonlinear converters with ZnGeP₂ allow to obtain radiation with tunable output wavelength from 2 μm up to 12 μm what presents an interest for applied spectroscopy.

Studies of ZnGeP₂ optical absorption spectra revealed existence of two mechanisms of optical losses: defect related absorption at 0.65 – 2.5 μm and "shadow" caused by second phase precipitates acting in whole crystal transparency range (0.65 – 12 μm).

It is found that the defect related absorption of the ZnGeP₂ crystals can be reduced down to acceptable level by post-growth anneals. For annealed crystals with a low density of precipitates (< 300 cm⁻²) the optical losses do not exceed 0.1 cm⁻¹ at 2 μm and 0.05 cm⁻¹ at 3-8 μm. Herewith the second phase precipitates turn out stable and remains responsible for optical losses in 3-8 μm region.

It was determined that this obstacle for production of high efficient ZnGeP₂ frequency converters caused by simultaneous action of composition deviation from stoichiometry and concavity of solid-liquid interface shape during crystal growth.

It was shown that IR thermovision technique is convenient for urgent indication of crystal volumes with high density of precipitates.

4. 6-th International Conference on Modification of Materials with Particle Beams and Plasma Flow, 23-28 September 2002, Tomsk, Russia

Report: "Formation of uniform point defect distribution in ZnGeP₂ single crystals at fast e-beam irradiation" by A.I. Gribenyukov, G.A. Verozubova, A.Yu. Trofimov, N.T. Yunda

ABSTRACT

The results of distribution profile calculations for point defects occurring in ZnGeP₂ samples under fast e-beam irradiation are presented using two different estimates of the binding energy of atoms in the crystal lattice. The use of a binding energy of 25.15eV derived from the averaged bond energies in the compound gives good agreement between calculated and observed irradiation defect distribution profiles. In contrast, we conclude that the value of binding energy for Zn atoms in ZnGeP₂ derived from data on nearest neighbour Zn-P bond strengths leads to an underestimate. . Approximation of the calculated irradiation defect profiles by Gaussian distributions allows us to define the irradiation regimes producing ZnGeP₂ samples with electrical non-uniformity less than 10 %

5. 6-th International Conference on Modification of Materials with Particle Beams and Plasma Flow, 23-28 September 2002, Tomsk, Russia

Report: "Interaction of native optically active defects of ZnGeP_2 with defects introduced by e-beam irradiation" by A.I. Gribenyukov, G.A. Verozubova, A.Yu. Trofimov, N.T. Yunda

ABSTRACT

Behaviour of optical absorption in non-linear single crystals ZnGeP_2 were studied under the effect of post-growth thermal anneal and e-beam irradiation. It was found that optical absorption spectra of as-grown and annealed materials in region 0.5-1.2 eV related to the deep donor level with energy $E \sim E_V + 0.9$ eV. Electron beam irradiation significantly changes the energetic structure of optically active defects. Irreversible changes of absorption spectra in region 0.5-1.2 eV were found under influence of e-beam irradiation and at low temperature post-irradiation anneals. These changes are explained by interaction of primary defects with irradiation ones

6. MRS Fall Meeting 2002, 2-6 December 2002, Boston, MA, USA.

Report: "Growth and characterization of epitaxial films of ZnGeP_2 " by G.A. Verozubova, A.I. Gribenyukov, M.C. Ohmer, N.C. Fernelius, J.T. Goldstein.

ABSTRACT

Semiconducting ZnGeP_2 is non-linear optical material highly attractive for radiation frequency conversion in the middle IR, particularly for creation of OPO pumped by 2 μ lasers. Volume and surface imperfections existed in ZnGeP_2 preclude from use these crystals in high power laser systems.

Physical properties of crystals grown from vapor can advantageously differ sometimes from those of the bulk ones. Here we report initial investigations on growth and characterization of ZnGeP_2 homoepitaxial films.

The technological parameters for experiments on ZnGeP_2 films growth were estimated by using calculations of equilibrium composition of gas phase in Zn-Ge-P-Cl system. The calculations show that the vapor phase in this system consists mainly of ZnCl_2 , GeCl_2 , GeCl_4 , and PCl . It was also found that efficiency of transporting agent decreases with increase of its concentration.

The ZnGeP_2 films were grown in a closed gas transport system with chlorine compounds used as transporting agents. The films were studied by X-ray methods, by microscopy, and by PL.

X-Ray powder analysis shows that CVD material consists only of one phase, namely, ZnGeP_2 with lattice parameters $a = b = 0.54656 \pm 0.00002$ nm, $c = 1.07114 \pm 0.00005$ nm.

Preliminary results of studies show that the grown films are more perfect than bulk crystals.

7. MRS Fall Meeting 2002, 2-6 December 2002, Boston, MA, USA.

Report: "Native point defect interaction in ZGP crystals under influence of e-beam irradiation" by A.I. Gribenyukov, G.A. Verozubova, A. Yu. Trofimov, A.W. Vere, C.J. Flynn.

ABSTRACT

Optical absorption in defect-related region of high-efficient non-linear ZGP crystals under e-beam irradiation and post-irradiation anneals has been investigated.

It was found partly irreversible changes of the absorption in spectral range 0.9-2.5 μ (0.5-1.3 eV) at effect of the irradiation and subsequent low-temperature anneals. Data obtained are in contradiction with vacancy nature of the ZGP absorption in the 0.5-1.3 eV range.

The least square fit for parameters of theoretical dependence of optical absorption cross-section to experimentally measured ZGP optical absorption coefficient spectra results in conclusion that the defect-related absorption in 0.5-1.3 eV region is caused by deep donor levels with energy position $E = E_V + 0.9$ eV.

Significant changes of the energy spectrum of dominant optically active centers have been indicated under influence of e-beam irradiation and post-irradiation anneals.

Founding on the optical absorption measurements data obtained for as-grown, annealed and e-irradiated ZGP crystals, model of point defects interaction taking in account both reversible

interactions such as formation of donor-acceptor pairs and irreversible interactions of quasi-chemical type has been proposed.

Behavior of optically active defects energy spectrum is discussed in frames of the model of interaction between the initial point defects and radiation ones.

Analysis performed showed that the best agreement with experimental data is reached when it is assumed that optical defect-related absorption in the 0.5-1.3 eV range related mainly to the disordering defect in cation sublattice of ZGP, namely, to atoms Ge substituting Zn.

Defect concentration profiles created by e-irradiation in ZGP crystals of different thickness were calculated. It was found the conditions providing uniformity of defect distribution on dept of irradiated ZGP samples.

The optimal e-beam irradiation flux, giving maximum of ZGP enlightenment, allowed us to reduce the defect-related absorption down to value 0.01 cm⁻¹ at 2 μ.

8. The 1-st International Symposium on Point Defect and Non-stoichiometry 2003 (ISPN 2003),
20-22 March, 2003, Sendai, Japan

Report: “ ZnGeP₂ growth in non-stoichiometry conditions” by G.A. Verozubova, A.I. Gribenyukov

ABSTRACT

This paper focuses on defect characterization in ZnGeP₂ and relationship “growth conditions - defect structure - physical properties”. Growth striation, precipitation of second phases and point defects are considered in this connection.

ZnGeP₂ were synthesized by original method allowing to produce more than 500 grams in one run. Two techniques were used to grow ZnGeP₂ single crystals. To produce bulk crystals with diameter 20-24 mm and length 100 mm a Vertical Bridgman method was used. Epitaxial films, 2-100 μ in thickness, were grown by chemical transport reactions with use Cl as transporting agent.

Growth striation in ZnGeP₂ can be easily found by optical microscopy of thin crystal plates. The growth striae do not show a strict periodicity, however several stable groups of striae can be distinguished with approximate periods 5-10, 60-180, 250-600 μ. Near-seed temperature measurement one second apart during several hours and comparison with striae periods showed that striation is related to thermal instability in growth setup.

Two types of precipitates can be observed in ZnGeP₂. The first ones, 3-10 μ in diameter, visible in optical microscope are related to non-stoichiometry of the melt and formed as a result of capture of excess components from the melt. The precipitates form lineage discontinuous structures oriented along the growth axis. A microprobe analysis indicates a complex structure of the precipitates: the central part is highly enriched in Ge, while the periphery has higher content of Zn and P as compared with ZnGeP₂ matrix. An increase of temperature gradient during growth allows produce ZnGeP₂ crystals free from this type of precipitates.

The revealed inhomogeneity substantially increase the optical losses in ZnGeP₂ crystals. Growth striation leads to non-monotonous change in optical absorption coefficient along the ingot. The high precipitate density gives 2-3-fold decrease in optical transparency in all transparency range of ZnGeP₂.

For crystals free from the precipitates the optical losses do not exceed 0.1 cm⁻¹ at 2 μ and 0.05 cm⁻¹ at the maximum transparency window 3-8 μ

The second type of precipitates is apparently related to retrograde solidus in ZnGeP₂. TEM shows a presence of much smaller, nanometer-sized precipitates with composition corresponded to GeP. Their small sizes show a slow rate of their formation, descended from decomposition of solid solution within a homogeneity range of ZnGeP₂.

Analysis of optical absorption spectra of as-grown, annealed and irradiated ZnGeP₂ crystals shows that optical absorption in 0.7-0.9 μ region is related to point defects of vacancy type. Mathematical treatment of the spectra and calculation of absorption cross-section in 1-2 μ region

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allow to presume a nature of point defects responsible for absorption in this region: deep donor level with energy $E_v + 0.9\text{ eV}$ is identified by us as substitution defect Ge_{Zn} .

Vapor growth of epitaxial layers of ZnGeP_2 shows more perfect structure as compared with bulk crystals. X-Ray analysis shows much more narrow half-widths of diffraction peaks and increased lattice parameters for the vapor grown material than that for bulk ZnGeP_2 grown from melt. This can be related to decrease in a vacancy concentration in the vapor grown material. Estimation gives that observed relative increase of the crystal cell volume of $4.9 \times 10^{-2} \%$ corresponds to decrease in summary vacancy concentration of $\sim 4 \times 10^{19} \text{ cm}^{-3}$.

Measured photoluminescence spectra for bulk ZnGeP_2 present a wide emission band in 0.7-1.5 eV region, consisting of two overridden elementary bands with maximums at 0.9 and 1.2 eV. An emitting transition with energy ~ 1.2 eV is usually attributed to point defects in anion sublattice (V_P), emission in 0.9-1.0 eV is related to disorder defects in cation sublattice (Zn_{Ge}). Luminescence spectra of film crystals show a presence only of one peak with maximum at 0.9 eV, corresponded to disorder defects in cation sublattice

9. The Second International Conference on Physics of Crystals: “Crystal Physics of 21 Century” devoted to M.P. Shaskol’skaya memory, 28-30 October 2003, MIS&A, Moscow.

Report “Anisotropy of optical absorption in ZnGeP_2 single crystals” by A.I. Gribenyukov, G.A. Verozubova, V. V. Korotkova, A. Yu. Trofimov, V. V.

ABSTRACT

Paper is devoted to the results of studies of optical absorption anisotropy in ZnGeP_2 single crystals grown in different laboratories developing nonlinear crystal technologies, namely:

- Lockheed Sanders(Martin), Nashua, N J, USA,
- DERA Malvern, UK,
- IOM SB RAS, Russia.

It was made a comparison data obtained and published in Lockheed Sanders as well as experimental studies carried out in INRAD (USA) and DERA Malvern (UK) on measurements ZnGeP_2 optical absorption with polarized light in samples grown in IOM SB RAS.

10. The Second International Conference on Physics of Crystals “Crystal Physics of 21 Century” devoted to M.P. Shaskol’skaya memory, 28-30 October 2003, MISA, Moscow.

Report: “Behaviour of optically active defects in crystals ZnGeP_2 under e-beam irradiation and isothermic anneals” by A. I. Gribenyukov, G. A. Verozubova, A. Yu. Trofimov

ABSTRACT

This contribution is a study of behaviour of the defect-related optical absorption spectra of ZnGeP_2 crystal under irradiation by fast (4 MeV) electrons and post-irradiation low-temperature thermal treatments.

A level of optical absorption in studied as-grown crystals is determined by deep levels with energy position $E = E_v + 0.9$ eV. Comparison of parameters of theoretical dependence of optical absorption cross-section [1] and experimentally determined values of optical absorption coefficient shows that the optically active centres can be attributed to deep donor levels.

No observed noticeable changes in energy spectra of the optically active defects under thermal treatment of ZGP crystals were found. It is shown that post-growth thermal annealing allows reduce the optical absorption coefficient at 2μ down to 0.1 cm^{-1} .

Electron beam irradiation of ZGP provides a higher decrease in optical absorption at 2.0μ as compared with thermal annealing. It is also found significant changes in the energy spectra of the optically active centres: the deep level donors with $E = E_v + 0.9$ eV disappear whereas defects with shallow levels occur. The defects appeared under e-beam irradiation (vacancies or their complexes) take part in optical transitions with the energy photons exceeding values of 1.4 eV.

Dependence between the optimal e-beam flux for the maximum enlightenment of ZnGeP_2 and initial absorption of ZnGeP_2 crystals is found. The optimal e-beam flux irradiation allows us to reduce the absorption down to values less than 0.02 cm^{-1} near 2μ .

Post-irradiation isothermal anneals show that changes in absorption occur in accordance with the second order reaction. The results of anneals do not accord with the simple vacancies nature of the optically active defects in ZnGeP_2 .

The optical absorption coefficient changes are discussed in frames of model of interaction between the pre-existing point defects and ones introduced by irradiation. Investigations performed allow conclude that the most probable origin of optical absorption in near IR region $0.5 - 1.2 \text{ eV}$ are substitution defects in cation sublattice - Ge_{Zn}

Information on patents and copy rights

At present the investigations of the ZnGeP_2 films properties are on initial stage.

In spite of encouraging data obtained by techniques accessible for the Project executors, there are not comparative data referred to optical damage threshold of the ZnGeP_2 films and substrates till now.

If the optical damage threshold for the ZnGeP_2 films turns out noticeable higher than for crystals grown from melt, only then the question related to patents and copy rights will be actual one.

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